

The effect of halide ion concentration on capacitor performance

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Abstract The effect of halide ion concentration on the capacitor performance was considered during this study. Iodide anion has been selected as the most profitable halide taking into account its electrochemical properties and environmental impact. Several concentrations of NaI were tested (from 0.25 to 5 mol L⁻¹ aqueous solutions) using as electrodes two commercial activated carbons and one KOH-activated carbon. Detailed electrochemical investigation by galvanostatic charging/discharging, cyclic voltammetry, and impedance spectroscopy confirmed the significant impact of iodide concentration on the supercapacitor behavior. The higher concentration of iodide affected especially the performance of positive electrode; increase of iodide concentration changed the potential range of positive electrode and its capacitance increased from 119 F g⁻¹ for 0.25 mol L⁻¹ NaI to 475 F g⁻¹ for 2 mol L⁻¹ NaI solution. The electrode capacitance measured in two-electrode system at current density of 2 A g⁻¹ ranged from 198 F g⁻¹ for 0.25 mol L⁻¹ NaI to 272 F g⁻¹ for 2 mol L⁻¹ NaI solution (capacitance expressed as average of the positive and negative electrode capacitances). It has been proved that 2 mol L⁻¹ alkali metal iodide solution is an optimal electrolyte for the capacitor based on KOH-activated carbon. High capacitance values and perfect stability (100 % retention) of such systems have been observed during long-term galvanostatic charging/discharging (15,000 cycles). In addition, satisfactory floating tests at extended voltage range (1.2 V) were performed.

Keywords Supercapacitor · Iodine · Carbon · Pseudocapacitance

1 Introduction

Nowadays, the world power and energy demands are still increasing, people are looking for new, economic, and reliable ways to produce and store the energy. Currently, many approaches are proposed to meet those requirements such as electrochemical capacitors, including supercapacitors and hybrid capacitors; many types of batteries; fuel cells; and some new ideas like redox-flow batteries [1–4]. From all these solutions, the most promising and fastest growing areas are lithium-ion batteries and supercapacitors [5]. Modern electrochemical capacitors perfectly fill the gap between capacitors and batteries; they are able to deliver high power peak and can cover energy demands of electrical devices [1, 5]. To strengthen the role of supercapacitors, researchers are looking for solution to increase the energy density of these devices without sacrificing high power properties. To meet this challenge, obviously energy and power of capacitors need to be increased. Newly proposed system should utilize well-organized carbon structures taking into account electrolyte ion's dimensions [5, 6]. Application of electrically conducting polymers (PANI, PPy, etc.) or some electroactive species being able to perform fast redox reactions like metal oxides (RuO₂, MnO₂, NiO, etc.) [7–9] could be another alternative. The performance of electrochemical capacitors can be also enhanced by the increase in their operation voltage. In this approach, many systems based on organic electrolytes and ionic liquids were proposed [10, 11]. The main drawbacks of these solutions are high costs of materials, safety issues, problems with conductivity, and

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corrosion. To meet the demand of the growing needs for cheap and environmental-friendly system, halide (Br^- , Cl^- , or I^-)-based supercapacitors were developed [12–14]. Among halides, iodine-based system seems to be the most promising solution because of the lowest environmental impact. Earlier, the positive effect of exploiting aqueous solution of potassium iodide was confirmed, and the high capacitance values were obtained [12, 15, 16]. This study focuses on performance optimization of carbon/iodide-based capacitor. The effects of iodide ion concentration and pore structure of carbon will be considered in detail.

2 Experimental

During electrochemical studies, various concentrations of NaI in aqueous solutions have been tested as electrolytes for redox-based supercapacitors. The investigations were carried out in two- and three-electrode cells, namely Swagelok® systems. Electrodes were composed of 85 wt% activated carbon, 10 wt% PVdF Kynar Flex 2801, and 5 wt% acetylene black SUPER C65. Two commercially available activated carbons, i.e., Norit SX2 and Norit DLC Super 30 have been used as active materials. In addition, KOH activation of Norit SX2 supplied an alkali-activated carbon named AAC. Specific surface area and pore size distribution of carbon materials have been characterized by N_2 adsorption/desorption at 77 K using Micromeritics ASAP 2020 instrument. The electrodes (8–10 mg) were prepared in the form of pellets (0.785 cm^2 ; mass loading of $10.2\text{--}12.7 \text{ mg cm}^{-2}$); placed on stainless steel current collectors; and then assembled in the Swagelok® cells made of Teflon®. To perform electrochemical characterization of such constructed systems, various techniques, i.e., cyclic voltammetry, galvanostatic charging/discharging, floating, and electrochemical impedance spectroscopy, have been used. All those experiments were performed using potentiostat/galvanostat VMP3 from BioLogic®, France. The current density and capacitance values were calculated per active mass of single electrode for both experiments performed in two- and three-electrode cells. For clarity, the following formula $C = (I \cdot dt)/dU$ has been used for capacitance calculation in the case of three-electrode cell whereas $C = 2(I \cdot dt)/dU$ for two-electrode cell. Obviously, the whole capacitor would have 25 % of the capacitance for single electrode. Good correlation has been found between the results obtained from three electrochemical techniques (cyclic voltammetry, galvanostatic charge/discharge, and impedance spectroscopy). Moreover, to estimate the stability of those systems, long-term galvanostatic cycling at 2 A g^{-1} as well as floating tests [17] at 1.2 V has been applied.

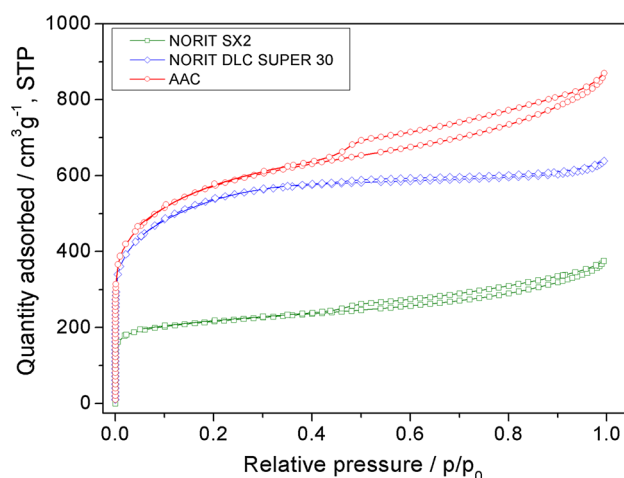


Fig. 1 Nitrogen adsorption/desorption isotherms at 77 K for selected carbons

3 Results and discussion

To estimate the impact of halide concentration, three carbons with different characteristics and specific surface area have been chosen. Figure 1 shows the isotherms of carbons selected to construct capacitor systems. Norit DLC super 30 has high specific surface area of $1,850 \text{ m}^2 \text{ g}^{-1}$ and highly microporous character. The second carbon, i.e., Norit SX2 has lower specific surface area ($850 \text{ m}^2 \text{ g}^{-1}$), and the small contribution of mesopores can be observed. AAC carbon shows the highest specific surface area about $1,950 \text{ m}^2 \text{ g}^{-1}$ and microporous character with a high contribution of mesopores. Specific surface areas of all carbons were calculated from BET isotherm. The choice of such different carbons allowed assessing the influence of carbon texture on the behavior of iodide-based capacitor.

Comparison of galvanostatic charge/discharge plots at 2 A g^{-1} (Fig. 2) shows strong influence of sodium iodide concentration on electrochemical behavior of AAC-activated carbon. The capacitance values of electrodes in this system range from 198 F g^{-1} for 0.25 mol L^{-1} NaI solution to 272 F g^{-1} for 2 mol L^{-1} NaI solution. Surprisingly, the capacitance value of 252 F g^{-1} for 5 mol L^{-1} NaI solution was remarkably lower than that for 2 mol L^{-1} NaI solution; it means that there is no linear increase of capacitance with iodide concentration and electrolyte conductivity. Specific conductivity of 0.5 mol L^{-1} NaI is equal to 72 mS cm^{-1} ; for 1 mol L^{-1} NaI, it is 160 mS cm^{-1} , whereas for 2 mol L^{-1} NaI and 5 mol L^{-1} NaI, the values are 275 and 330 mS cm^{-1} , respectively. The efficiency of capacitor charging/discharging is more than 100 %, which indicates a gradual extension of potential range for positive electrode. This suggests that iodide-based systems are suitable for long-term cycling

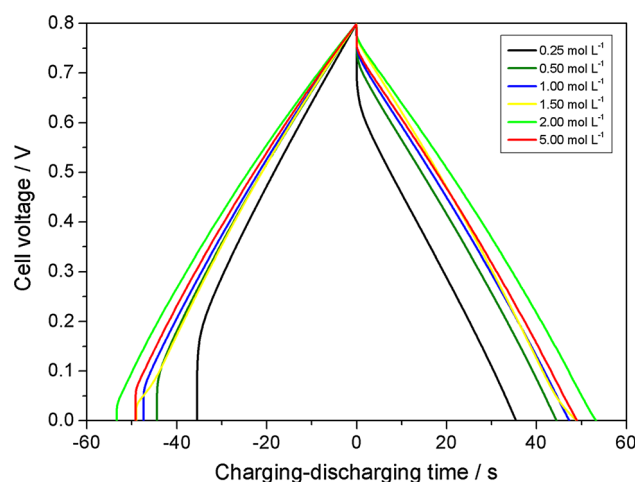


Fig. 2 Galvanostatic charging/discharging of capacitor with AAC electrodes at 2 A g^{-1} for different NaI concentrations

processes. It can be also observed that with increase of electrolyte concentration, the value of ohmic drop is decreasing, which correlates with increase of conductivity for more concentrated medium. Although for 5 mol L^{-1} NaI solution, the association of ions can play some effect, for other carbons with less-developed surface area (e.g., Norit SX2), more than two times lower capacitance values were obtained; for Norit DLC super 30, there was no significant effect of concentration change, and high ohmic drop was noticed. In case of Norit SX2, some impacts due to concentration changes were observed. The capacitance values were ranging from 90 F g^{-1} for 1 mol L^{-1} NaI to 113 F g^{-1} for 2 mol L^{-1} NaI solution; also, lower ohmic drop with increase of solution concentration was observed. Such a behavior indicates that for iodide-based capacitor system, the best performance requires high surface area originating from suitable micropore structure and good mobility that comes from mesoporous character. It is noteworthy to mention that redox species of iodine, i.e., I_3^- and I_5^- , eventually IO_3^- , can have dimensions from 0.63 to 1.8 nm; hence, for their useful accommodation in the bulk of electrode, supermicropores and small mesopores are indispensable.

Figure 3 shows comparison of cyclic voltammograms of AAC-based capacitors with capacitance values expressed per one electrode. At low scanning rate (1 mV s^{-1}), some irregular box-shaped curves were observed. This behavior can be correlated with occurrence of pseudocapacitive properties of iodine-based system (better pronounced at low regime). The highest capacitance value of 283 F g^{-1} was obtained for electrode operating in 2 mol L^{-1} NaI solution. With increase of scan rate, the box shape disappears, and the character of system is slightly resistive. The box-shaped retention can be observed up to 20 mV s^{-1} with the capacitance of 256 F g^{-1} for 2 mol L^{-1} NaI

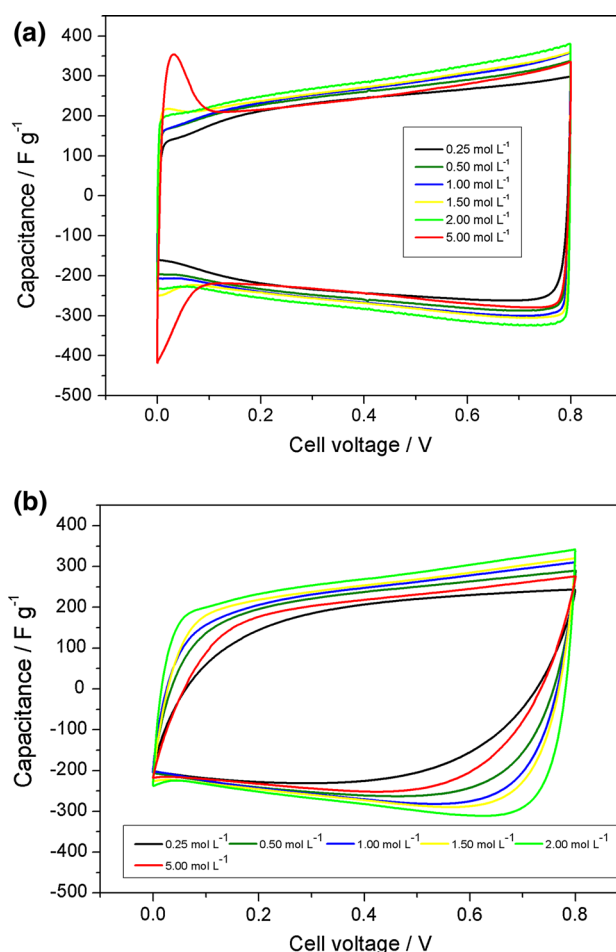


Fig. 3 Capacitance values of different concentrations of NaI with AAC as electrode material from voltammetry characteristics at 1 mV s^{-1} (a) and 20 mV s^{-1} (b). Capacitance values expressed per electrode

solution. The shapes of curves are slightly different from those obtained on gold collectors, reported previously [12, 15]. On stainless steel current collectors, there is no sudden increase of capacitance, which can be observed on gold current collectors, but there is gradual increase of capacitance with the increasing voltage [12, 15]. For high 5 mol L^{-1} concentrated NaI solution at low voltage value, a redox peak can be observed; this peak originates from pseudocapacitive behavior of the positive electrode (Fig. 3). Similar behavior was observed for Norit SX2 carbon which is the precursor of ACC. In case of strictly microporous carbon (Norit DLC super 30) for all scanning rates, the shapes of capacitance/potential curves for different concentrations of electrolytes were identical. Comparison of all carbons for 2 mol L^{-1} NaI at the same scan rate (1 mV s^{-1}) shows an increase of electrode capacitance from 138 F g^{-1} for Norit SX2, to 141 F g^{-1} using DLC super 30 and reaching up to 283 F g^{-1} for AAC-based capacitor electrodes. This behavior clearly indicates the

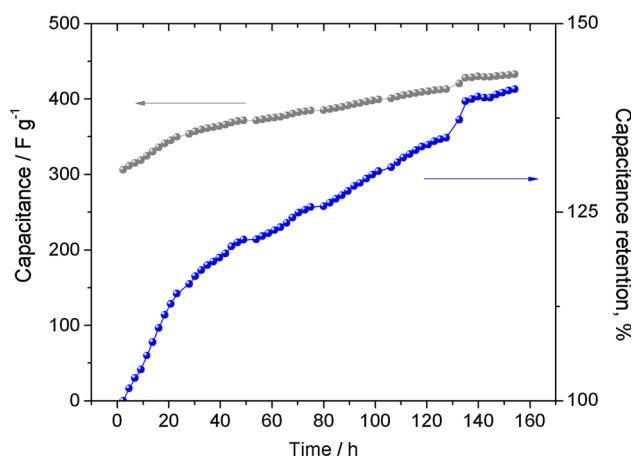


Fig. 4 Capacitance values and capacitance retention during floating tests at 1.2 V for 2 mol L⁻¹ NaI solution with AAC electrode material

importance of mesoporous carbon structure in iodine-based systems. Certainly, mesoporosity plays a perfect role to transport reactive species, whereas microporosity is responsible for the formation of the electrical double layer that improves the capacitance of the whole system. Also as mentioned before, the beneficial impact of increase of conductivity with rising concentration cannot be omitted.

The long-term cycling at 2 A g⁻¹ confirmed the ability of these systems to work without capacitance fading. During such cycling, a negligible fluctuation of capacitance can be observed, but even after 15,000 of charging/discharging cycles, these systems did not show any loss of capacitance, but on the contrary, a remarkable increase in the capacitance. It might be partly explained by progressive penetration of active material by electrolyte; however, the incorporation of iodine into structure of carbon should be considered. Figure 4 shows the results from floating at 1.2 V during 150 h. For the duration of this experiment, the significant increase of capacitance has been also confirmed. After the experiment, the systems were disassembled, and no sign of corrosion was observed on separator, electrodes, and surface of current collectors. This result confirms that carbon/iodide system can safely work in higher voltage without danger of leak or cell damage.

Electrochemical impedance spectroscopy showed beneficial impact of the increase of iodine concentration in all systems. From the Nyquist plot shown in Fig. 5a, it can be observed (Fig. 5a inset) that ESR values become lower with the increasing concentration from 0.89 Ω for 0.25 mol L⁻¹ NaI solution to 0.18 Ω for 5 mol L⁻¹ NaI solution. Also when concentration increases to 2 mol L⁻¹, the value of semicircle decreases, which indicates that for more concentrated solution, the access to active surface is easier. However, in case of 5 mol L⁻¹ NaI solution, the

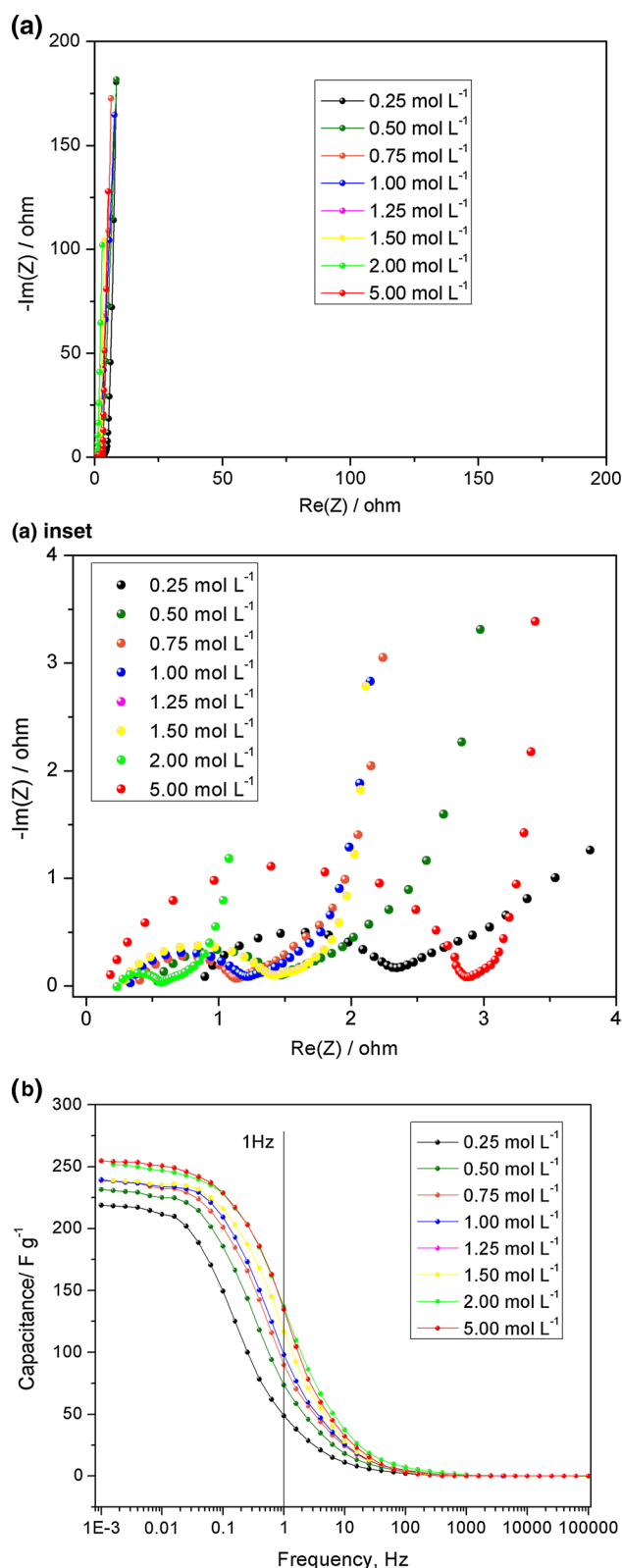


Fig. 5 Electrochemical impedance spectroscopy Nyquist plot (a) and dependence of capacitance versus frequency (b) for different concentrations of NaI with electrode materials containing AAC as active material

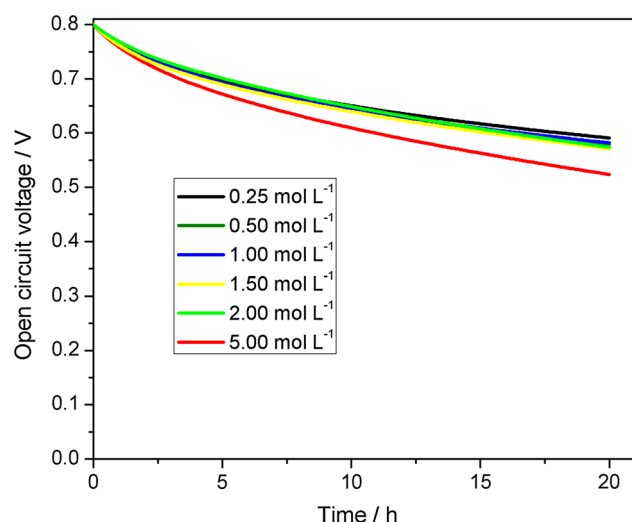


Fig. 6 Open-circuit voltage for 20 h for different concentrations of NaI with AAC electrode material

semicircle value is the highest, and it clearly indicates that at this concentration, there might be some problems with the transport of iodine species due to molecular collisions

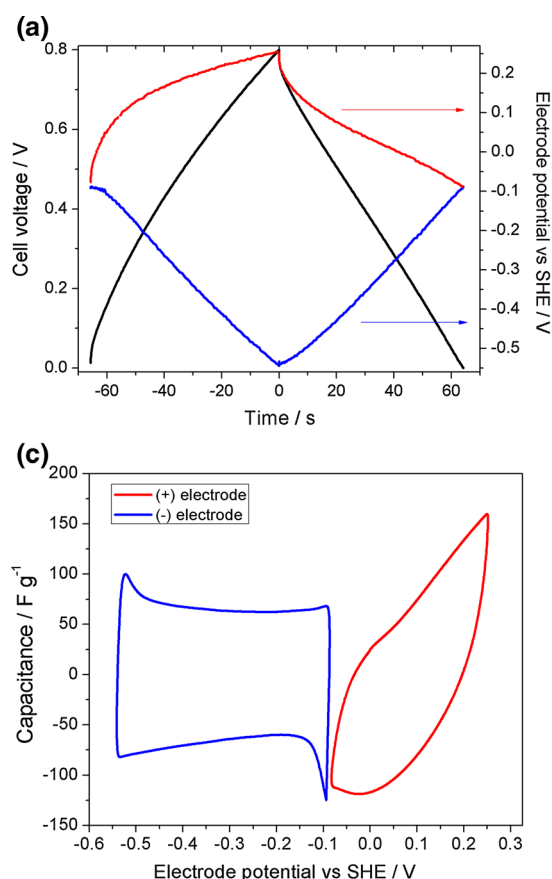
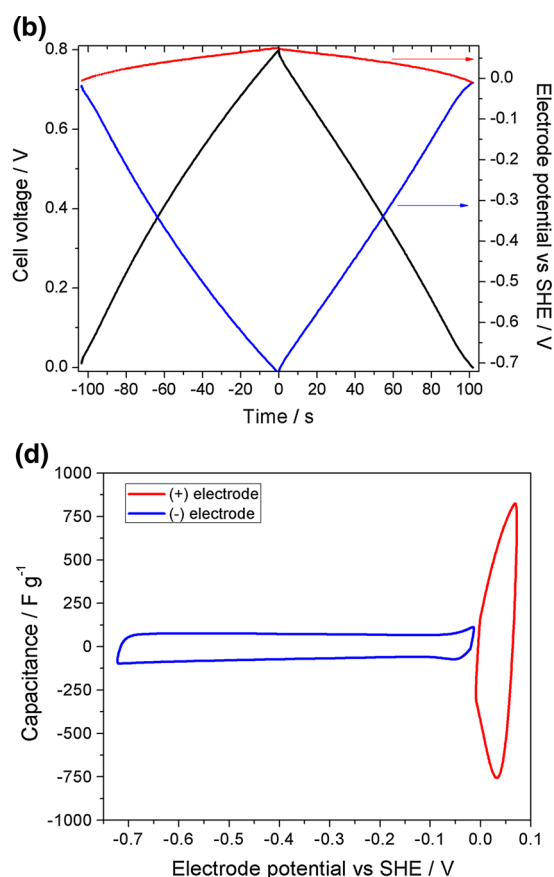


Fig. 7 Galvanostatic charge/discharge at 0.5 A g^{-1} for 0.25 mol L^{-1} (a) and 2 mol L^{-1} (b) NaI electrolytes; capacitance values of positive and negative electrode for 0.25 mol L^{-1} (c) and 2 mol L^{-1} (d) NaI

(association) or some steric hindrance at carbon/electrolyte interface and in pores of active material. Nyquist plot showed good capacitive properties of all systems; more concentrated electrolytes reach lower values on imaginary part of impedance. Figure 5b shows dependence of capacitance versus frequency; for all systems especially in the low-frequency range, the positive impact of electrolyte concentration increase was noticed. In 2 mol L^{-1} NaI electrolyte, the maximum capacitance at 0.1 Hz was 228 F g^{-1} , but even for 1 Hz , capacitance value was about 137 F g^{-1} , which proves a good charge propagation during fast charge/discharge.

Figure 6 shows the comparison of voltage fade, while the system is not upon forced polarization (self-discharge). After 20 h of open circuit, the system containing 0.25 mol L^{-1} NaI solution keeps the highest voltage value of 0.6 V . For other electrolytes, except 5 mol L^{-1} NaI solution, similar values of voltage were maintained (from 0.59 to 0.57 V). For the highest concentration of electrolyte, the voltage value after 20 h was 0.52 V .

Three-electrode cell investigation on capacitors with Norit SX2 carbon shows increasing disproportion in capacitance values between negative and positive electrode



electrolyte from the voltammograms at 5 mV s^{-1} with Norit SX2 carbon as active material

Table 1 Capacitance values for AAC carbon in various concentrations of NaI solutions

Capacitance values (expressed in F g^{-1} per one electrode) for AAC carbon in NaI solutions						
Technique	0.25 mol L^{-1}	0.5 mol L^{-1}	1 mol L^{-1}	1.5 mol L^{-1}	2 mol L^{-1}	5 mol L^{-1}
Charge/discharge at 0.2 A g^{-1}	234	257	266	272	287	263
Charge/discharge at 2 A g^{-1}	198	235	248	256	272	252
Cyclic voltammetry at 1 mV s^{-1}	231	253	262	269	283	254
Impedance spectroscopy at 1 Hz	49	74	98	116	137	135

with the increasing electrolyte concentration. From galvanostatic charge/discharge plots presented in Fig. 7a and b, the changes of operating potential values of electrodes can be observed. With the electrolyte concentration increase the operating potential range of positive electrode narrowed from 350 mV for 0.25 mol L^{-1} NaI electrolyte to 100 mV for 2 mol L^{-1} NaI electrolyte. This result confirms the presence of iodine redox reaction on positive electrode which gives huge capacitance value of 476 F g^{-1} for 2 mol L^{-1} NaI electrolyte. Unfortunately, the capacitance of full system is limited by low performance of negative electrode. In Fig. 7a, nonlinear shape of positive electrode characteristic can be observed. It indicates that even in diluted solutions, there are some contributions of capacitance from carbon/iodine interface. Figure 7c, d shows the narrowing of working potential range and the increasing capacitance on positive electrode with the increasing electrolyte concentration. Capacitance values expressed in F g^{-1} obtained from different techniques for AAC carbon material are presented in Table 1.

4 Conclusion

In summary, the approach to optimize halide-based capacitor system has been presented. Iodide was selected as the most appropriate halide taking into account electrochemical properties as well as environmental aspect. The results confirmed the beneficial effect of electrolyte concentration increase on capacitor performance and high capacitance values (300–475 F g^{-1} for positive electrode) were obtained. However, because of different mechanisms of charge accumulation, i.e., mainly faradaic on positive electrode and electrostatic on negative one, the capacitance of the whole capacitor is equal to 75 F g^{-1} , being limited by the negative electrode with lower capacitance. Moreover, comparison of these systems working with different carbon materials revealed the highest capacitance values for AAC-activated carbon. It has been proven that there is no linear relation between iodide concentration and performance of these systems. Capacitor working with 5 mol L^{-1} NaI electrolyte showed worse performance than the system operating in 2 mol L^{-1} NaI solution.

Correlation of capacitance versus frequency showed that even at 1 Hz, these systems can provide more than 100 F g^{-1} . Lack of capacitance fading during long-term cycling at 2 A g^{-1} and the increasing capacitance during floating tests at higher voltage (1.2 V) proved that capacitor based on iodine species are extremely stable.

This outcome gives the idea that iodine-based systems can be still enhanced by proper selection of activated carbon material, which will join the benefits of high specific surface area of micropores and good transport properties originated from mesopores. It proves that supercapacitor utilizing cheap components, stainless steel current collectors, and environmental-friendly electrolyte, i.e., NaI (but also KI) aqueous solutions, are a good candidate for the world's growing energy-storage demands.

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